THE TREATABILITY OF PERCHLORATE IN GROUNDWATER USING ION EXCHANGE TECHNOLOGY

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The application of ion-exchange processes to the removal of perchlorate from contaminated drinking water requires basic information associated with the selectivity of perchlorate relative to the common anions found in natural waters. Separation factors have been calculated at three different temperatures for numerous strong base resins. These resins vary as a function of (1) matrix (polystyrene, polyacrylic, polyvinylpyridine), (2) functional group (trimethylamine, dimethylethanolamine, methylpyridine, trialkylamine), and (3) porosity (microporous, macroporous, isoporous). With these separation factors, predictions were made as to the behavior of the resins in an ion-exchange process for the removal of the perchlorate ion from groundwater of varying composition. By validating these predictions with experiments using several different types of resins, the computer models used to make these predictions were then used to model the behavior of many different types of resins in differing operational conditions.

Resin Characteristics

Binary isotherms were constructed for seventeen commercially available strong-base anion-exchange resins with variable compositions. These resin variables tested were polymer matrix, functional group and percent cross-linking. Figures 1 through 3 are diagrams of the molecular structure of the three polymer matrices tested: polystyrene, polyacrylic, and polyvinylpyridine.

The different functional groups present on the resins studied are represented in Figure 4. Typical Type I strong-base resins have a trimethyl functional group. By enlarging or replacing various components of this basic functional group, resins with different characteristics are obtained.

There are also differences in the microstructure of the resins. The amount of cross-linking between the polymer chains can be varied to produce resins of differing characteristics. The amount of cross-linking usually varies between 2% to 20% with 8% cross-linking being typical. Resin flexibility decreases as percentage cross-linking increases. Low percentage cross-linking leads to flexibility, which allows the resin to swell upon immersion in water to a greater degree compared with high percentage crosslinking.

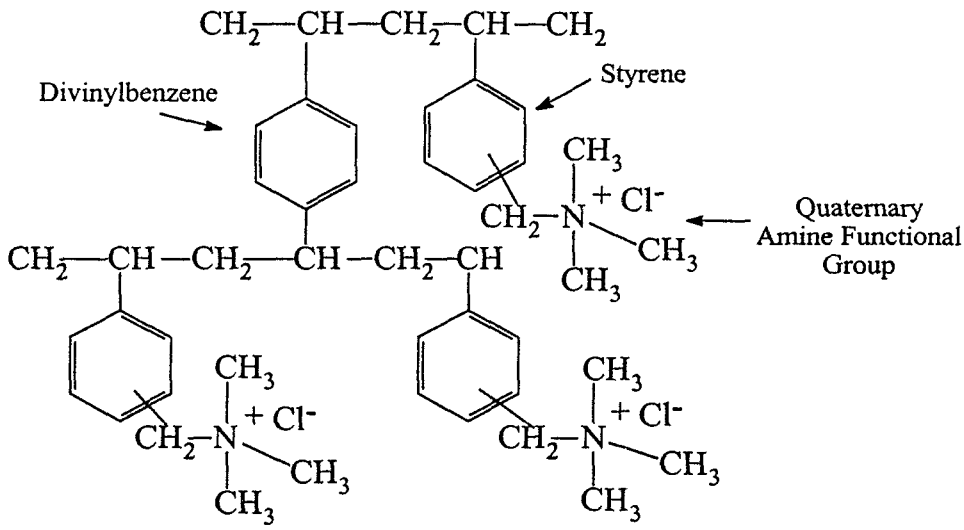

Figure 1. Diagram of a polystyrene, Type I, trimethyl-quaternary amine, strong base anion-exchange resin in the chloride form.

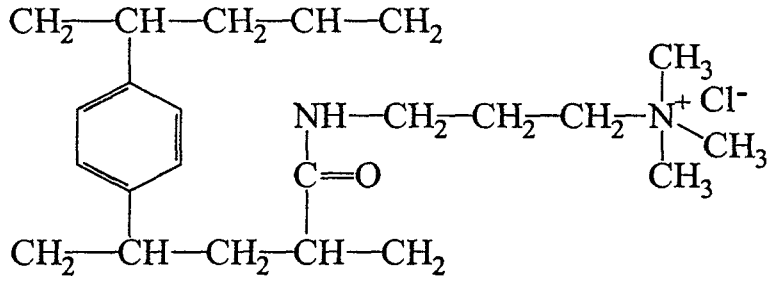

Figure 2. Diagram of a polyacrylic, trimethyl quaternary amine, strong-base anion-exchange resin in the chloride form.

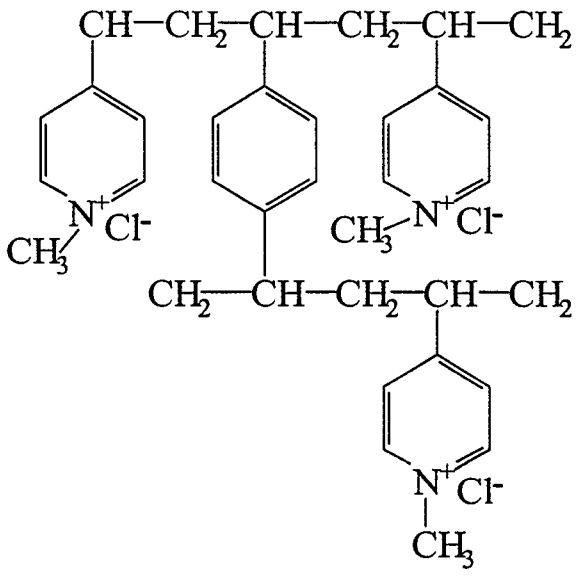

Figure 3. Diagram of a chloride-form polyvinylpyridine, strong-base anion-exchange resin with methylpyridine quaternary amine functional groups.

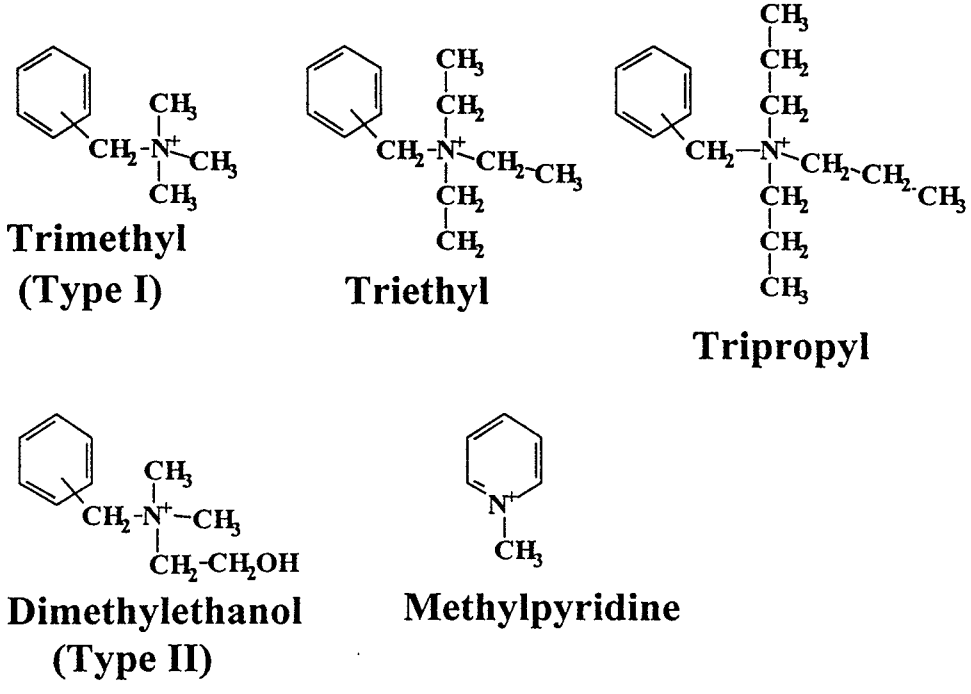

Figure 4. Diagram of the different quaternary amine functional groups studied in this research.

Isotherm Procedure

The separation factors were determined by using equilibrium batch isotherms. During the equilibrium batch isotherm procedure, a mass of air-dried chloride-form resin was added to 100 mL of solution containing 0.005 meq L^{-1} perchlorate (500 μg L^{-1}) and 4.995 meq L^{-1} chloride (177 mg L^{-1}). This mixture was shaken in a water bath maintained at ±1°C of the target temperature for 24 hours. At this time a sample was taken for the measurement of both perchlorate and chloride. This procedure was repeated for varying masses of resin resulting in different equilibrium concentrations. At least five different equilibrium perchlorate concentrations spread over the range of 5 to 50 μg L^{-1} were used in the construction of isotherms in this study. The isotherm was constructed by plotting $y_{ClO_4^-}$ (equivalent fraction of ClO_4^- on the resin) vs $x_{ClO_4^-}$ (equivalent fraction of ClO_4^- in solution) in the equivalent fraction range (0 - 0.014) of interest in this study.

Separation Factors

Table 1 presents the effect that differences in cross-linking, matrix composition, and functional group can have upon the chloride-perchlorate separation factor. The polyacrylic resins have a low affinity for perchlorate relative to the other two matrices tested. For the polystyrene resin there is a large increase in the separation factor as the size of the functional group is increased from trimethyl to tributyl. There is also a small increase in separation factors as the percentage of divinylbenzene cross-linking increases.

Table 1. The effect of various resin characteristics upon perchlorate separation factors.

Characteristic	Resin	Separation Factor
Cross-Linking	IRA-400	125
Cross-linking	IRA-402	100
Matrix	Polyvinylpyridine	275
Matrix	Polystyrene	125
Matrix	Polyacrylic	6
Functional Group	Trimethyl	125
Functional Group	Triethyl	>1000
Functional Group	Tripropyl	>1500

Kinetics

Figure 5 is a plot of perchlorate affinity (separation factor) versus equilibration time for 1-, 3- and 7-day tests. As can be seen, there is no effect of time upon the polystyrene trimethyl quaternary amine resin (Sybron ASB-1). In contrast, the polystyrene tripropyl quaternary amine resin (Sybron SR-7) has not reached equilibrium even after seven days of mixing. Apparently, these resins with very high separation factors are so hydrophobic that the transport of water becomes the limiting step in achieving equilibrium. It is possible that resins with very high separation factors may not perform as well as resins with lower separation factors due to this transport problem.

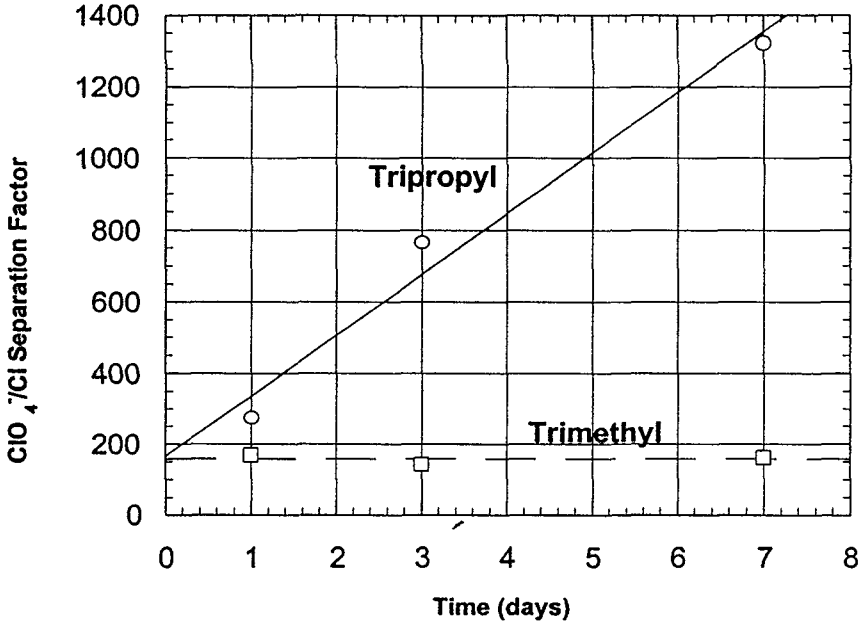

Figure 5. The effect of equilibration time upon the ClO_4^--Cl^- separation factor. After seven days, the perchlorate separation factor is still increasing for the tripropyl resin, which has not reached equilibrium.

Effect of Temperature

The binary isotherms were conducted at equilibration temperatures of 20°, 40° and 60°C. The percent change of the ClO_4^--Cl^- separation factor with temperature for all seventeen resins tested is shown in Figure 6. Resins 11 and 13 have polyacrylic type matrices while all others have either polystyrene or polyvinylpyridine. The two polyacrylic resins show little change with temperature while for the remaining resins there is an approximately 30% decrease in the separation factor for both the 20°-40°C and the 40°-60°C temperature changes with an overall decrease of 60% for the 20°-60°C change. This trend indicates that the ion-exchange reaction is exothermic and, as temperature increases, the equilibrium constant (separation factor) decreases. This trend is important for both exhaustion and regeneration. The warmer the temperature, the lower the separation factor and the shorter the run length before exhaustion. At higher temperature, the lower the separation factor, the smaller the volume of solution needed for regeneration. To maximize the efficiency of a system, the exhaustion phase should be at cool temperatures and the regeneration phase should be at elevated temperatures.

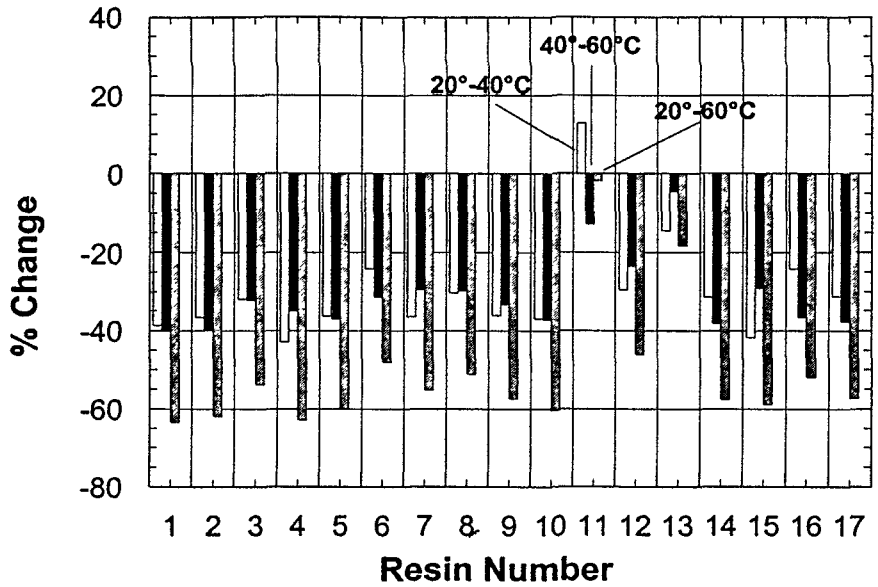

Figure 6. Percent change in the ClO_4^--Cl^- separation factor with temperature for the seventeen resins tested. The polyacrylic resins (11,13) showed little change while the polystyrene and polyvinylpyridine resins exhibited approximately 30% decrease with each 20°C increase in temperature.

Predictions and Corroboration

Perchlorate was loaded onto two different types of resins, a polyacrylic (Amberlite, IRA-458) and a polystyrene (Sybron, ASB-2), to a fractional loading of 0.007. This loading is similar to that for the removal of perchlorate from groundwater with a perchlorate concentration of 100 μg L^{-1} and a sulfate concentration of 50 mg L^{-1}. The perchlorate loaded onto the resins was then eluted off the resins with a 1 N NaCl solution to simulate the regeneration of a resin column. Figures 7 and 8 show the actual elution of perchlorate from the IRA-458 and ASB-2 resins, respectively, compared to the predicted elution profile using a multicomponent equilibrium program (EMCT Windows) developed at the University of Houston. The actual data contains tailing at the end of the elution curve representative of mass transfer limitations. The computer prediction was reasonably accurate in estimating the concentration of perchlorate in the eluent and the amount of regenerant solution needed to elute the perchlorate off of these two different types of resins.

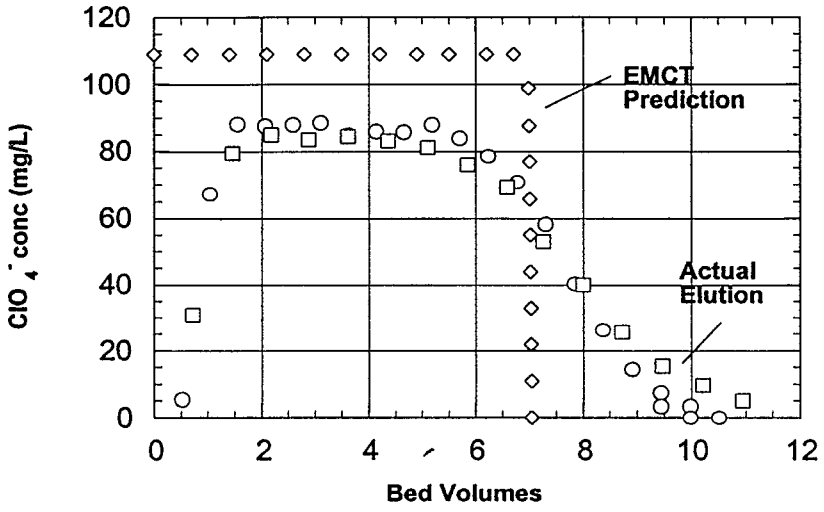

Figure 7. Comparison of the actual and predicted elution of perchlorate from IRA-458 resin using 1 N NaCl solution

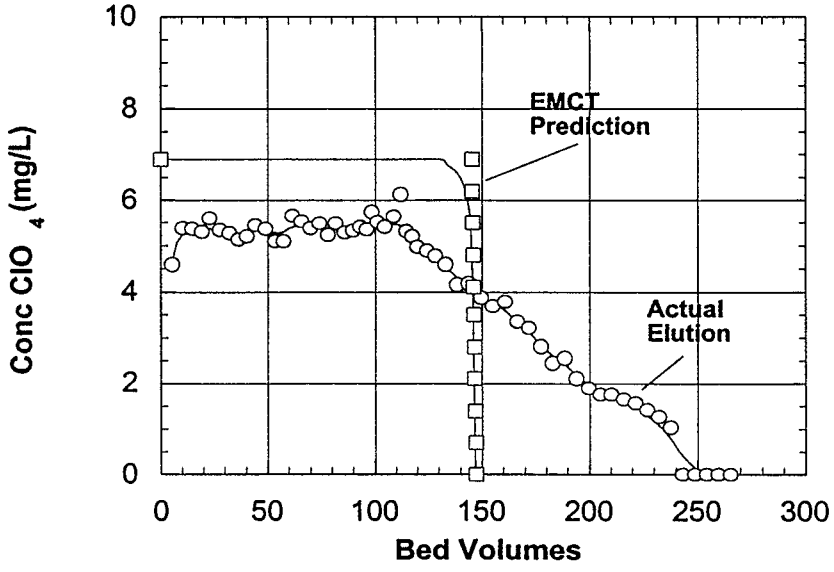

Figure 8. Comparison of the actual and predicted elution of perchlorate from ASB-2 resin using 1 N NaCl solution.

Because the EMCT Windows program requires constant separation factors and homogeneous presaturation, a more advanced computer model, IX WINDOWS PRO™, produced by Cathedral Peak Software, was used to model the behavior of the resins using water of varying components and concentrations. This model uses the equilibrium stage concept to simulate the exhaustion and regeneration of a column and the condition of each stage can be followed through many exhaustion and regeneration cycles. Thus, various experimental conditions can be modeled and conditions predicted to be impractical can be avoided without extensive experiments. This is especially important in situations where exhaustion requires tens of thousands of bed volumes over periods of weeks and months. Figure 9 shows the effluent concentration of perchlorate as predicted by the computer program over 60 exhaustion and regeneration cycles. To experimentally perform 60 cycles of a resin to a run length of 2000 bed volumes would require over 4 months time.

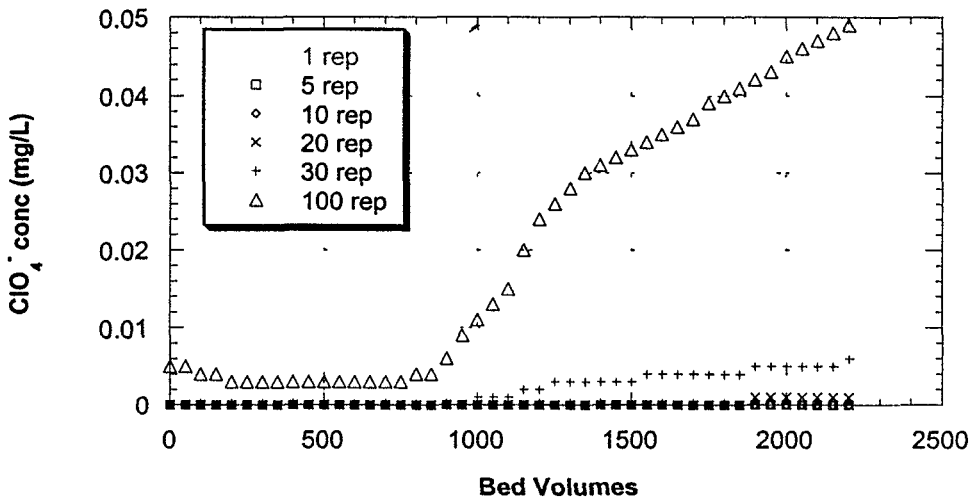

Figure 9. Computer modeling of the effluent concentration of perchlorate over numerous exhaustion/regeneration cycles using a groundwater of typical concentration

The water used in the model had a composition of 0.001 meq L^{-1} perchlorate, 1 meq L^{-1} sulfate, 2 meq L^{-1} bicarbonate, 0.4 meq L^{-1} nitrate and 0.8 meq L^{-1} chloride. Perchlorate separation factors of 110 and 44 were assumed for exhaustion at 25°C and regeneration at 60°C, respectively. Regeneration was counter-current using 7.5 bed volumes (27.4 lbs NaCl ft^{-3} resin) of 1 N NaCl solution. The model indicates that there will be negligible leakage of perchlorate for the first 30 exhaustion/regeneration cycles, but that eventually the resin will accumulate perchlorate to the extent that the leakage of perchlorate will become excessive.